<International Research Center for Elements Science>Organotransition Metal Chemistry

International Research Center for Elements Science – Organotransition Metal Chemistry –

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Scope of Research

This laboratory aims at establishment of new synthetic methodologies and new functional materials by designing well-defined catalysts based on transition metal chemistry. New concepts and ideas of molecular-based catalysts are accumulated by mechanistic investigations using experimental methods such as spectroscopy and kinetic techniques as well as theoretical methods. The research subjects include: (1) development of novel organotransition metal systems for catalysis based on precise ligand design, and (2) preparation of π-conjugated polymers by using direct arylation.

KEYWORDS

Transition Metal Complex
Homogeneous Catalyst
Reaction Mechanism
Low-coordinate Phosphorus Ligand
π-Conjugated Polymer

Selected Publications

Wakioka, M.; Nakamura, Y.; Wang, Q.; Ozawa, F., Direct Arylation of 2-Methylthiophene with Isolated $[PdAr(\mu\text{-}O_2CR)(PPh_3)]_n$ Complexes: Kinetics and Mechanism, *Organometallics*, **31,** 4810-4816 (2012).

Wang, Q.; Wakioka, M.; Ozawa, F., Synthesis of End-capped Regioregular Poly(3-hexylthiophene)s via Direct Arylation, *Macromol. Rapid Commun.*, **33,** 1203-1207 (2012).

Nakajima, Y.; Ozawa, F., Redox Chemistry of Bis(phosphaethenyl)pyridine Iron Complexes, *Organometallics*, **31,** 1203-1207 (2012).

N-Alkylation of Amines with Alcohols Catalyzed by Bis(phosphaethenyl)pyridine Iridium and Ruthenium Complexes

Phosphaalkenes with P=C bonds exhibit strong π-accepting ability toward transition metals owing to their extremely low-lying π* orbitals. We recently demonstrated that PNP-pincer type phosphaalkene ligands, 2,6-bis(2-phosphaethenyl)pyridines (BPEP-Y; Y = Ph, H), successfully stabilize reactive complexes in a low oxidation state. In this study, we found that BPEP-Y complexes effectively catalyzed *N*-alkylation of amines with alcohols in high selectivity.

The Ir(I) complex [IrCl(BPEP-H)] (**1**), in conjunction with a strong base (CsOH), catalytically converted primary amines into secondary amines (eq 1). This catalysis was adaptable to substituted anilines and aliphatic amines and to several kinds of aliphatic alcohols. The formation of tertiary amines was not detected even in the presence of excess alcohols. In contrast, in the presence of KH_2PO_4 instead of CsOH, the same complex catalyzed *N*-alkylation of secondary amines to give tertiary amines (eq 2). Different from **1**, BPEP-Ph Ru(0) complex **2** predominantly catalyzed dehydrogenative coupling of alcohols and amines to form imines (eq 3).

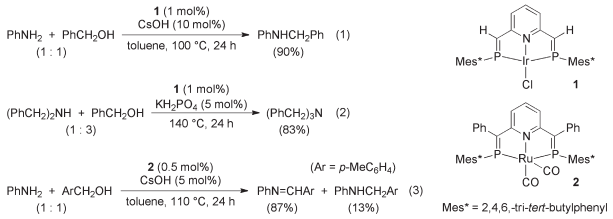
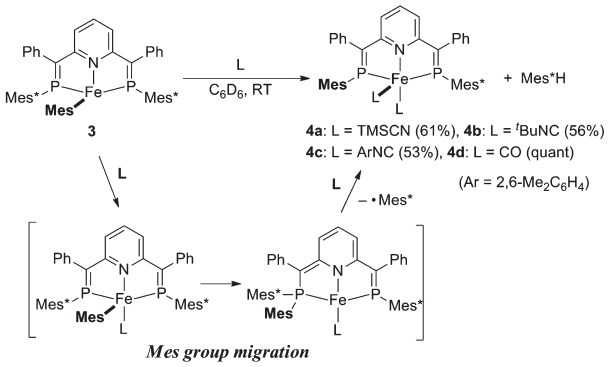


Figure 1. Structures and catalytic activities of **1** and **2**.

Reactions of Bis(phosphaethenyl)pyridine Fe(I) Complexes with π-Acid Ligands

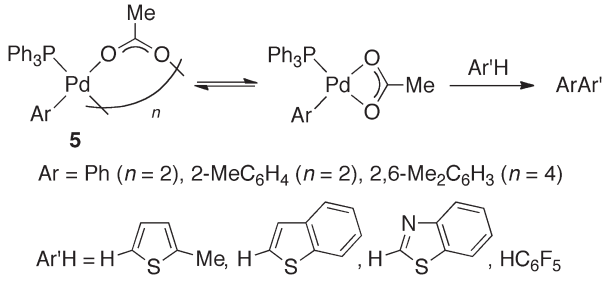
Low-coordinate Fe(I) complexes are rare for their instability, and their reactivity has been poorly understood. Recently, we have demonstrated that BPEP-Ph successfully stabilizes the Fe(I) mesityl complex **3**. In this study, we revealed unusual reaction behavior of **3** in the presence of π-acid ligands such as isocyanides and CO. Complex **3** underwent a structural rearrangement upon treatment with small excess π-acid ligands at ambient temperature, leading to the formation of Fe(0) complexes (**4a-d**). Interestingly, one Mes* group on the P=C bonds was replaced by the Mes group, which originally existed on the Fe center, probably via the migration of Mes group to the phosphorus atom (Scheme 1).



Scheme 1. Reaction of [FeMes(BPEP)] (**3**) with π-acid ligands.

Direct Arylation of Heteroarenes with Isolated Arylpalladium Complexes

Dehydrohalogenative coupling of heteroarenes with aryl halides catalyzed by palladium complexes (so-called direct arylation) has attracted a great deal of attention as an alternative to conventional cross-coupling reactions. Recent theoretical studies have suggested that this catalysis involves an arylpalladium carboxylate intermediate, which undergoes C–H bond cleavage of aromatic compounds. However, isolated complexes that are reactive to C–H bond cleavage have been extremely limited. In this work, we found that arylpalladium complexes $[PdAr(\mu\text{-}O_2CMe)(PPh_3)]_n$ (**5**) react with various heteroarenes (Ar'H) to afford direct arylation products (ArAr') in high yields (Scheme 2). Kinetic and structural examinations indicate that **5** is interconverted with the monomeric complex $[PdAr(O_2CMe\text{-}\kappa^2O)(PPh_3)]$ in solution, which reacts with heteroarenes.



Scheme 2. Reaction of $[PdAr(\mu\text{-}O_2CMe)(PPh_3)]_n$ (**5**) with various heteroarenes (Ar'H).